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**Pr DOPED YBCO FILMS PRODUCED BY PULSED LASER
DEPOSITION (POSTPRINT)**

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Pr Doped YBCO Films Produced by Pulsed Laser Deposition

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ABSTRACT

Pr doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ targets with composition $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-d}$ where $x = 0.0001, 0.001, 0.01, \text{ and } 0.1$ were prepared from oxide powders and used to deposit thin films by pulsed laser deposition using conditions previously optimized for pure $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$. The Pr dopant was found to be dispersed throughout the film by secondary ion mass spectrometry and the doped films had an increased density of nanoparticles on the surface. The pinning force of the doped samples was found to decrease with increasing concentration of Pr; however, several concentrations displayed pinning forces that surpassed pure YBCO. At 0.01% Pr concentration, the doped film displayed a significant enhancement over pure $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ for nearly the full range of 0 – 9 T. This study was conducted in order to determine a method of doping $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ to achieve high in-field critical current densities while allowing the processing conditions to remain unchanged.

INTRODUCTION

$\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ (YBCO) in the form of a biaxially aligned film on a buffered metallic substrate is currently being pursued as a high temperature superconductor (HTS) coated conductor for a variety of power applications. Some of the applications under consideration, such as motors and generators, will subject coated conductor to large magnetic fields where the performance of YBCO is suppressed¹. Although a critical current density (J_c) of $\sim 10^6 \text{ A/cm}^2$ is regularly attained in YBCO thin films under self-field conditions, magnetic fields in excess of 1T applied along the c-axis direction tend to reduce the J_c by an order of magnitude. Therefore, further improvement to the J_c is desired in order to use YBCO coated conductor in the full spectrum of high field applications as well as to minimize the size and weight of the power systems.

One possible method of achieving the desired $J_c(H)$ values is to incorporate well-dispersed, artificial, magnetic flux pinning centers into the YBCO lattice²⁻⁷. These pinning centers can consist of nonsuperconducting particulates²⁻⁴ or secondary superconducting phases⁵⁻⁷. Doping YBCO with rare earth (RE) elements can lead to the formation of both types of pinning centers. Nonsuperconducting particulates form when the RE elements react to form a nonsuperconducting phase, while secondary superconducting phases form when other RE elements substitute for yttrium in the crystal lattice. Due to the difference in ionic radius between the other RE elements and Y, replacement atoms may cause strain induced improvements. Modest improvements can be achieved with substitution in quantities exceeding 10% of Y; however, introducing RE substituents in such quantities may necessitate additional processing steps or re-optimization of the deposition parameters. Identifying potential dopants that can optimize the performance of YBCO films without changing the deposition conditions would be ideal.

The use of minute quantities of RE dopants may avoid process alteration. Although substituting rare earths into the yttrium sites in the YBCO structure can provide the proper size of pinning center, many rare earths (e.g. Sm, Eu, Gd, etc) require concentrations of greater than 10% and even then often provide only modest improvements. To achieve the desired pinning while maintaining the small size of pinning center and the minute doping concentration, a RE, such as La, Ce, or Pr, that has been shown to degrade the performance of YBCO in concentrations >10% could be used. The nature of the pinning provided by the substitution could be due to the inclusion of nonsuperconducting particles in addition to or in lieu of strain induced improvements. Previous results obtained through Tb and Ce substitution in quantities $\leq 1\%$ have shown some improvement of J_c ⁷.

Pr has been noted in the literature as forming a REBCO phase that is non-metallic^{8,9}. When Pr is partially substituted for Y, the T_c is lowered with increasing Pr concentration up to 50% at which point the material becomes nonsuperconducting^{10,11}. At the time of writing this paper, a few percent of Pr doping of bulk YBCO has demonstrated some minor improvements to performance¹², but none has been demonstrated in thin films. The work presented here provides an initial demonstration that the incorporation of very minor additions ($\leq 1\%$ of Y) of Pr into high quality YBCO thin films provides significant improvements of the films' in-field current densities at 65 K to 77 K, an expected operating temperature range for HTS machinery^{1,13}. Furthermore, enhancements were achieved in films deposited under the same conditions as the pure films. Although processing such small quantities raises concerns that the inclusions may not be well dispersed, it was found that the substituent was dispersed throughout the film and led to an increase in nanoparticles.

EXPERIMENT

Thin films of $(Y_{1-x},Pr_x)Ba_2Cu_3O_{7-d}$ were produced by PLD using conditions previously optimized for pure YBCO. PLD targets were prepared with the composition $(Y_{1-x},Pr_x)Ba_2Cu_3O_{7-d}$ where $x = 0.0001, 0.001, 0.01, \text{ and } 0.1$ from the precursor powders of Y_2O_3 , $BaCO_3$, CuO , and Pr_2O_3 (all nominally 99.99+% pure). Initial targets, with compositions of $x = 0.001, 0.01, \text{ and } 0.1$ were made by first preparing powders with compositions $YBa_2Cu_3O_{7-d}$ and

(Y_{0.9},Pr_{0.1})Ba₂Cu₃O_{7-d}. Final compositions were made by diluting the (Y_{0.9},Pr_{0.1})Ba₂Cu₃O_{7-d} powders with the YBa₂Cu₃O_{7-d} powder before the final reaction at 940°C. Further targets were made directly from oxides without diluting. The powders were dried, mixed, and calcined twice, once at 850°C and again at 880°C. Targets for use in pulsed laser deposition (PLD) were then pressed, fully reacted and sintered at 940°C until they reached a density of at least 80% of the theoretical density.

The depositions were performed on single crystal strontium titanate (STO) and lanthanum aluminate (LAO) substrates. A Lambda Physik LPX 305 KrF excimer laser ($\lambda=248$ nm) was used at a repetition rate of 4 Hz and a laser fluence of ~ 3.2 J/cm². The base pressure in the chamber was $< 6 \times 10^{-6}$ Torr. During the deposition the chamber pressure was maintained at 300 mTorr with 99.999% pure oxygen. The sample temperature during deposition was 775°C. After deposition, an in-situ oxygen anneal was performed at 500°C and 1 atm for 30 minutes.

Critical transition temperature (T_c) and magnetic J_c measurements were made with a Quantum Design Model 6000 Physical Property Measurement System with vibrating sample magnetometer attachment (VSM). The T_c s of the films were determined magnetically using an ac susceptibility technique with some additional resistive measurements. Film thicknesses were measured by a KLA Tencor P-15 profilometer and were typically $\sim 0.3 \mu\text{m}$.

DISCUSSION

AC Susceptibility data taken from 0.01%, 0.1%, 1%, and 10% Pr doped films deposited on LAO are shown in figure 1. With the exception of the 10% doped film the onset T_c s of the minutely doped films ranged between 90.1 K and 91.8 K which is comparable to that of the reference YBCO film. The increase in T_c with increasing concentration of Pr points to the dopant having a negligible effect on T_c at concentrations of $\leq 1\%$. When the concentration was increased to the 10% level, the Pr doped films showed a marked decrease in T_c to 86.6 K consistent with published results in powders^{8,10}.

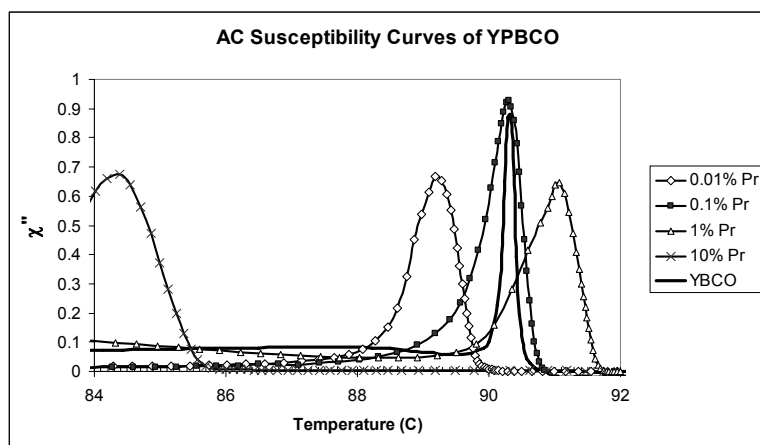


Figure 1. AC susceptibility curves from 0.01%, 0.1%, 1% and 10% Pr doped YBCO taken at a field of 1.0 Oe.

With the dopants being present in such small quantities in the YBCO films and incorporation of the dopant by powder processing, a question arises as to the distribution of the dopants. To determine the dopants location, secondary ion mass spectrometry (SIMS) was used at multiple locations on a sample to measure the elemental composition through the cross-section. Figure 2 shows a depth profile measured for a film with the composition $(Y_{0.999}, Pr_{0.001})Ba_2Cu_3O_{7-d}$. The graph indicates that the dopant was found throughout the entire cross-section in amounts close to the measurement limit of the detector. This indicates that the processing method is adequate to achieve good dispersion, especially with dopant concentrations of $\geq 0.1\%$. The Cu concentration in the figure appears to increase beyond the interface. This increase is an artifact due to the mass interference between ^{63}Cu and $^{47}Ti^{16}O$ in the STO substrate.

Although the SIMS data provides evidence of the presence of Pr in minor quantities and its dispersion throughout the film, it does not give indication of the dispersion on the microscopic level. Figure 3 displays the surface microstructure of a pure YBCO film and a $(Y_{0.999}, Pr_{0.001})Ba_2Cu_3O_{7-d}$ film. The SEM images show that the films both have a high density and similar grain size. Also, nanoparticles are present on the surfaces of both samples. The nanoparticulates, however, have a significantly higher density and are more dispersed on the doped film. The increase in nanoparticles on the surface of the doped film suggests that at least a fraction of the dopants form secondary phases instead of site substituting with the Y.

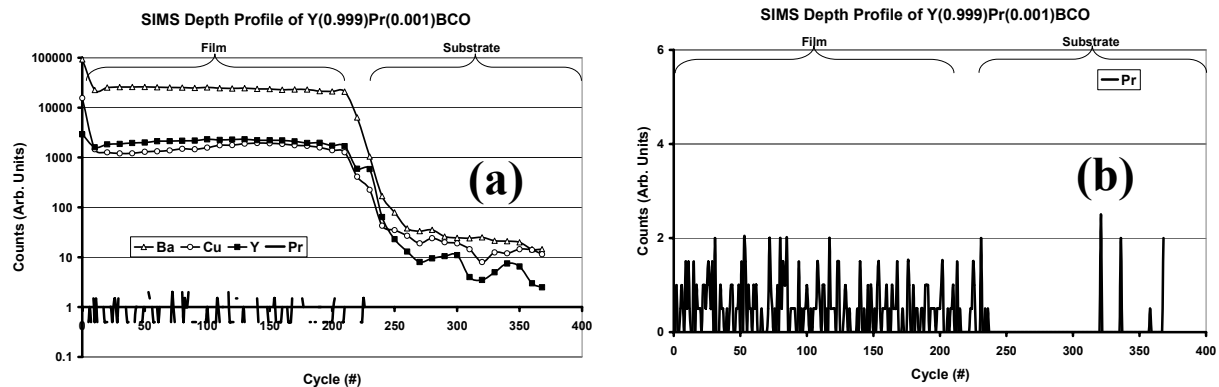


Figure 2. SIMS data for the minutely doped films shows the presence of the minor dopants in the $(Y_{0.999}Pr_{0.001})Ba_2Cu_3O_{7-d}$ films in log scale and normal scale.

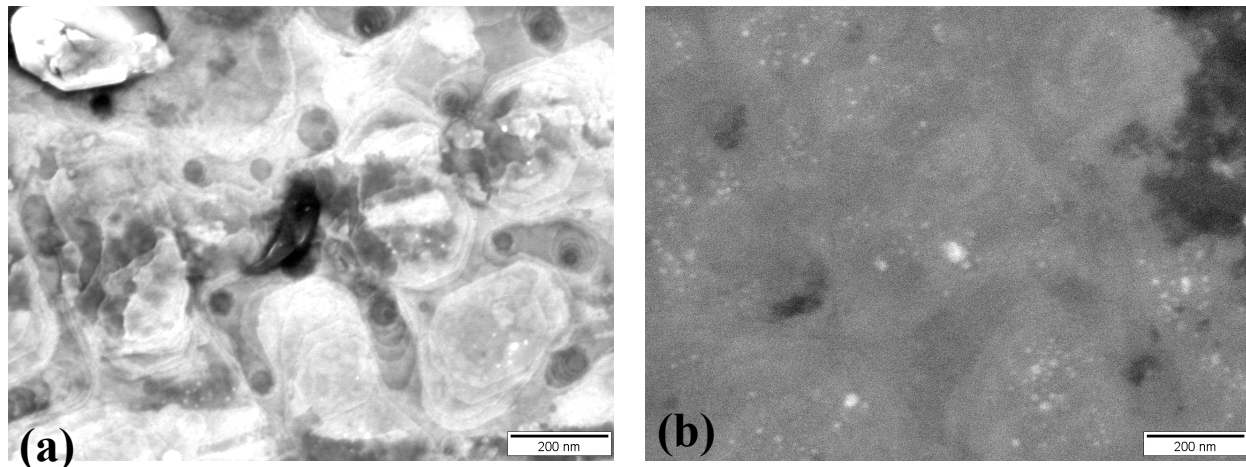


Figure 3. SEM images of the surface for a YBCO and a $(Y_{0.99}Pr_{0.01})Ba_2Cu_3O_{7-d}$ film.

Sample	10% Pr doped	1% Pr doped	0.1% Pr doped	0.01 % Pr doped	YBCO
J_c (MA/cm ²)	0.67	2.2	2.0	2.2	2.2

Table 1. J_c values for each sample in an applied field of 100Oe obtained by VSM measurements.

J_c and pinning force data was obtained for samples deposited simultaneously with the samples measured by AC susceptibility. These samples were likewise deposited on LAO substrates; however, results on STO were similar. Table 1 lists the critical current density for each of the doped samples and pure YBCO. Each sample, with the exception of (Y_{0.9}, Pr_{0.1})Ba₂Cu₃O_{7-d}, have $>10^6$ A/cm² J_c at 100Oe. Figure 4 displays pinning force plots for these same samples at 77K and 65K, where the pinning force was calculated by $F_p = J_c \times B$. The curves shown for each of the concentrations are representative of the results obtained from multiple depositions. Multiple depositions were made to verify repeatability of the results; in the case of (Y_{0.9}, Pr_{0.1})Ba₂Cu₃O_{7-d}, a new target was processed as well to ensure consistency. As an example, the initial deposition of YBCO with minutely doped Pr (1%) showed little difference from YBCO, but subsequent depositions consistently demonstrated enhanced performance. Samples with composition (Y_{0.9}, Pr_{0.1})Ba₂Cu₃O_{7-d} were also included for comparison with previously published work.

At 77K and 65K, the 0.01% doped film displayed the best pinning improvement among the tested concentrations with a substantial increase over pure YBCO for nearly the full range of measured field. At 77K the 0.1% and 1% concentrations were found to show similar performance to pure YBCO, while at 65K, the 0.1% Pr doped film still displayed enhanced pinning. The results for 10% Pr samples were consistent with previously published work regarding the degrading nature of these elements as inclusions in the YBCO structure. With the exception of 1% Pr at 77K, pinning force was found to decrease with increasing concentration of Pr for the doped films.

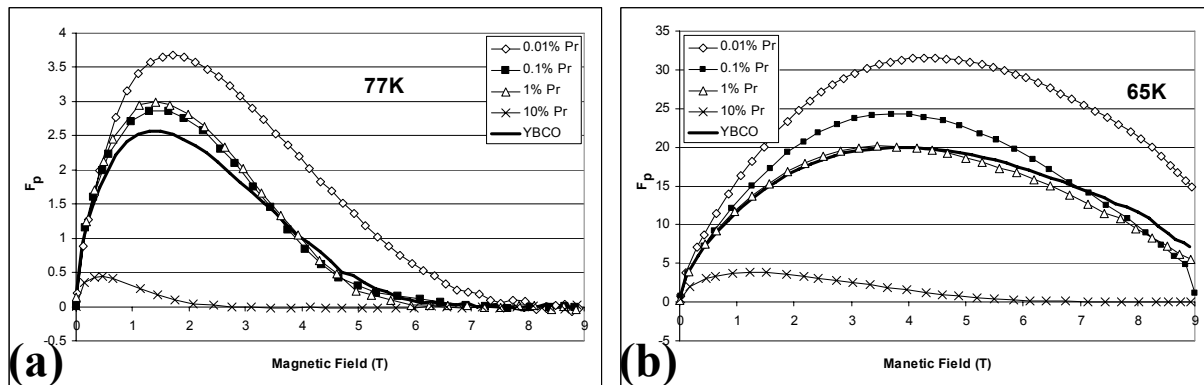


Figure 4. Pinning force plots for pure YBCO and the minutely doped (Y_{1-x}RE_x)Ba₂Cu₃O_{7-d} films (x = 0.0001, 0.001, 0.01, 0.1) at (a) 77K and (b) 65K.

CONCLUSIONS

YBCO was doped with minute amounts of Pr, a deleterious rare earth at higher concentrations, and thin films produced by pulsed laser deposition. Results demonstrate that minute doping of YBCO with this rare earth can significantly improve J_c over wide range of applied magnetic field. The $(Y_{0.9999}RE_{0.0001})Ba_2Cu_3O_{7-d}$ composition appears to be the best of those presently attempted at 77K and 65K. In every case, the same deposition parameters were used as that for pure YBCO with no need for re-optimization of the films. At this point, it is apparent that the Pr substituent is well dispersed in the films; however, microstructural characterization by TEM is necessary to determine how the dopant is distributed within the film as a $PrBa_2Cu_3O_{7-d}$, a secondary phase inclusion, or both.

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